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13. ABSTRACT (Maximum 200 words) O-Alkyl N-substituted phosphoramidic acids fragment thermally with the release of an alkyl metaphosphate. Best results are obtained with large N-substituents. The dipolar form is the actual species undergoing fragmentation. When substrates with OH groups (alcohols, phosphorus acids, solids like silica gel or zeolites, cellulose and fabrics) are present in the medium, phosphorylation takes place. The process was extended to include the generation of alkyl metathiophosphates by fragmentation of related phosphoramidothioates, similarly useful in thiophosphorylation. When phenyl replaced O-alkyl (as in phenylphosphonamidic acids), fragmentation occurred to release phenyldioxophosphorane, also useful in phosphorylation of OH species. A new approach in 7-phosphanorbornene chemistry involves synthesis of derivatives with very large P-substituents. These were prepared from phospholes bearing these substituents. The phosphanorbornenes are potential precursors of low-coordination phosphoryl species. Aryl phosphenites were generated by thermolysis of 1,3,5,2,4,6-trioxatriphosphorinanes, and their reactivity to OH species studied. The OH species was shown both to add to the P=O group and to displace the OR group.			
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**A NEW TECHNIQUE FOR GENERATION OF 3-COORDINATE  
PHOSPHORYL SPECIES: APPLICATIONS IN SURFACE MODIFICATION**

*FINAL REPORT*

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August 12, 1996

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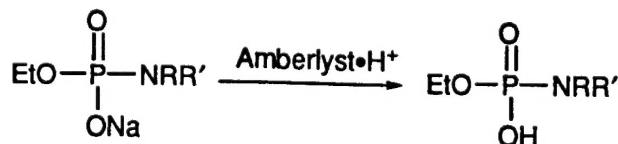
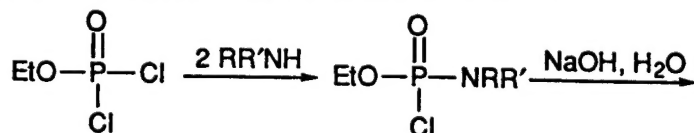
## I. PURPOSE OF THE RESEARCH PROGRAM

This project may be viewed as a continuation of earlier studies<sup>1</sup> sponsored by Army Research Office on new techniques for the generation of the transient, highly reactive family of low-coordination phosphoryl species and their use as potent phosphorylating agents. The earlier studies concentrated on an approach involving fragmentation of derivatives of the 7-phosphanorbornene and 2,3-oxaphosphabicyclo[2.2.2]octene ring systems, and to a lesser extent of alpha-oximinophosphonates. The present project was designed to explore the fragmentation of O-alkyl N-substituted phosphoramidic acids as a source of alkyl metaphosphates, and to investigate practical utility of metaphosphates so generated in the phosphorylation of OH groups. This includes the use not only of alcohols but also of the OH groups of phosphorus acids (to form anhydrides) and the OH groups on the surface of solids (silica gel, zeolites). Included also was the possible application in flameproofing of cellulosic fabrics through covalent attachment of the phosphorus group to the surface. It was also planned to investigate extension of the general concept of the phosphoramidic acid fragmentation to the generation of alkyl metathiophosphates and of aryl dioxophosphoranes. It was anticipated that some continuing work on our earlier approach to metaphosphate generation by thermal fragmentation of derivatives of the 2,3-oxaphosphabicyclo[2.2.2]octene ring system would be included. This Final Report summarizes the progress made on many of these projects. Since full experimental detail has already been published, or is in process of being published, only the highlights of the research will be presented here, with references to the published work.

## II. MAJOR ACCOMPLISHMENTS

### A. Phosphoramidic Acids as Precursors of Alkyl Metaphosphates.

It was considered that the major objective of this grant period was to demonstrate the effectiveness and scope of the proposed new technique for the generation of alkyl metaphosphates based on the thermolysis of monoalkyl esters of phosphoramidic acids. This required first developing a useful synthetic method for these acids, which is outlined below<sup>2</sup>.

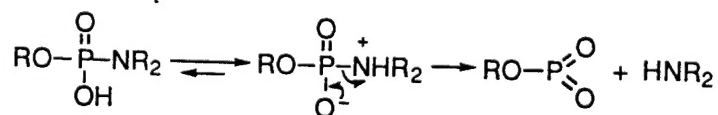


Results were generally quite good with yields in each step around 60-80%. Since the starting material is the commercially available phosphorus oxychloride, the method has practical value. Several structures were prepared and characterized during this study as shown below.

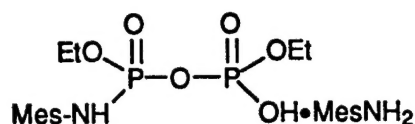


<u>R</u>	<u>R'</u>	<u>R''</u>
Et	Et	Et
Et	Ph	H
Et	H	Mesityl
Et	H	1-Adamantyl
Menthyl	H	1-Adamantyl
Menthyl	H	Ph
Menthyl	H	Mesityl
sec.-Butyl	H	Mesityl
2-Bornyl	H	Phenyl

It was established that the thermolysis technique for generating alkyl metaphosphates was indeed useful, provided the phosphoramidic acid had large bulky groups on nitrogen. Preferred were 1-adamantyl and mesityl. With these substituents the kinetics of the fragmentation reaction were established to be first order, in keeping with the unimolecular mechanism shown below.



With smaller N-substituents, mixed first-order, second-order kinetics were observed. However, even these phosphoramidic acids were effective as phosphorylating agents. With the aid of kinetic isotope effects based on nitrogen<sup>3</sup>, it was shown that it was not the neutral version (1) of the phosphoramidic acids, but the dipolar form (2) that underwent the fragmentation. If no trapping agent for the metaphosphate was present in the thermolysis medium, the released metaphosphate proceeded to attack unreacted phosphoramidic acid, yielding the mixed anhydrides of type 3.

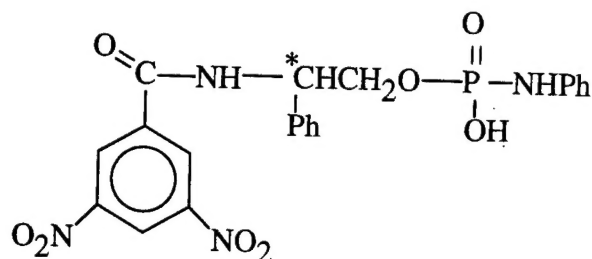


The conditions worked out for the fragmentations are quite simple, and somewhat dependent on the substituents present. A variety of solvents may be used but no OH or NH groups can be present. Some examples of useful solvents are toluene, benzene, chlorobenzene, acetonitrile, chloroform, 1,2-dichloroethane, tetrahydrofuran, and dimethyl sulfoxide. Fragmentations are generally complete in 1-2 hour at temperatures in the range 70-90<sup>0</sup>.

If a hydroxy-bearing trapping agent is present in the medium, anhydride formation is suppressed or eliminated, and the product is a dialkyl phosphate. The method is of practical value for the synthesis of mixed dialkyl phosphates. A number were prepared by this route and isolated for spectral characterization.

In addition to the phosphorylation of the OH groups of alcohols, our new method is applicable to the phosphorylation of the acidic OH group of phosphoric and other phosphorus acids, thus leading to a valuable type of substitution pattern in the pyrophosphate system. we prepared, for example, the new compound O-ethyl O'-thymyl pyrophosphate by this method.

The OH group found on the surface of certain solids can also be phosphorylated by this new technique<sup>4</sup>. The reaction has been successfully performed on silica gel, zeolites, and powdered cellulose. In every case, proof is provided that the phosphate group is bonded to the surface by solid-state <sup>31</sup>P NMR, using the cross-polarization magic angle spinning technique. The P content of phosphorylated solids is typically in the range 1-3%. The phosphorylated silica gels, also prepared previously by the technique involving fragmentation of derivatives of the 2,3-oxaphosphabicyclo[2.2.2]octene ring system to generate the metaphosphate<sup>1</sup>, have been shown to have useful properties in liquid chromatography<sup>2</sup>. For example, greatly improved separations of amines, usually difficult unless conducted by the reverse phase method, have been achieved, and excellent separations of petroleum fractions were performed<sup>2</sup>. Of special interest is the possibility that with optically active groups on the phosphate moiety the modified silica gel might possess the capability of performing resolution of racemic compounds. Several phosphoramidic acids with optically active O-substituents were prepared, and fragmented in the presence of HPLC-grade silica gel. The acids prepared for this study contained N-phenyl groups; the optically active O-substituents were 2-bornyl, ethyl mandelyl, and N-(3,5-dinitrobenzoyl)-2-phenylglyciny (as in 4). The latter was specifically designed to conform with the optically active substituents placed on silica gel in the commercially available resolving agents developed by Pirkle.



Columns were prepared with the phosphorylated silica and several typical racemic mixtures were passed through. In one case (benzoin), preliminary results suggest that resolution may have occurred, since a pure (by HPLC) sample gave two peaks on the chromatogram. However, the critical test of determining the optical activity of the eluted material remains to be performed.

The OH groups on zeolites also can be phosphorylated by metaphosphates<sup>4</sup>. These products could be of interest as catalysts, since zeolites are well known to perform many catalytic tasks. A collaboration has been arranged with Prof. Paul Kropp, University of North Carolina, to test catalytic effects of some of the phosphorylated solids. Some preliminary tests in our own laboratory, however, were not encouraging. Several model reactions were performed in the presence of zeolite Y phosphorylated with (+)-menthyl metaphosphate, but no significant catalytic effects were noted. The reactions studied included hydride reductions of carvone and of benzalacetone, hydride reduction of the epoxide of cholesterol and of styrene, and Diels-Alder reactions of 1-acetoxybutadiene with N-phenylmaleimide and with p-quinone.

During the course of the work on silica gel and zeolites, we discovered that phosphorus acids could react directly with the OH groups on the surface to give the same phosphates as formed with metaphosphates<sup>5</sup>. This is an extremely practical process, and prompts continued evaluation of the solids as catalysts.

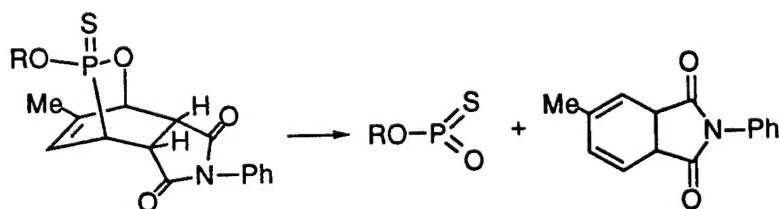
Another potential application of the new phosphorylation technique is in the area of flame proofing of cellulosic fabrics. It was reasoned that the free OH groups on cellulose would be phosphorylated if the fabric was placed in a medium where the phosphoramidic acid fragmentation was taking place. Many flame proofing agents are phosphorus compounds but generally they are present as additives and not as covalently bound functions. When bound, the phosphorus group should more effectively resist removal by washing. It was successfully demonstrated that cellulose was given a high degree of flame resistance when phosphorylated by exposure to O-ethyl N,N-diethylaminophosphoramidic acid as a source of ethyl metaphosphate. The



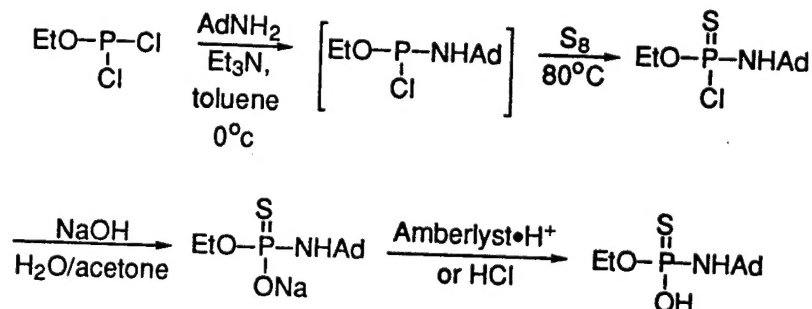
cellulose did not burn but simply charred, in such a way as to leave a grid of carbonized fibers. Several attempts were made to arrange for the proper testing of the effectiveness of this new technique under the proper controlled conditions. Of note was the interest shown by the U.S. Army Natick Laboratories, where testing of flame proofed fabrics is conducted. This facility was visited and discussions held on the possibility of a cooperative project to evaluate the new method. Definite interest was shown in this method and in the success of the preliminary flame experiments. As of this writing, however, the Natick Laboratory has not been able to respond with a plan for further experimentation. It is hoped that this will occur in the future, and that the work on this new method can be continued.

#### B. Generation of Metathiophosphates from Alkyl N-Substituted Phosphoramidothioates.

An extension of the phosphoramidic acid fragmentation process to thio derivatives was made as a possible source of alkyl metathiophosphates. The generation of alkyl metathiophosphates has only been accomplished by one other method, developed earlier in this Laboratory under ARO sponsorship<sup>6</sup>.

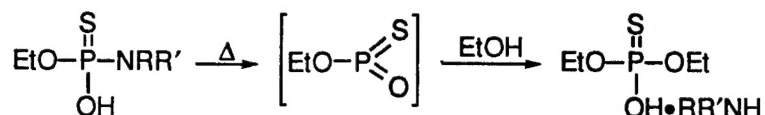


The proposed new method would be much more practical since the starting material is available from a much simpler synthetic path. The reactions we have used to synthesize a typical starting material are shown below<sup>7</sup>.

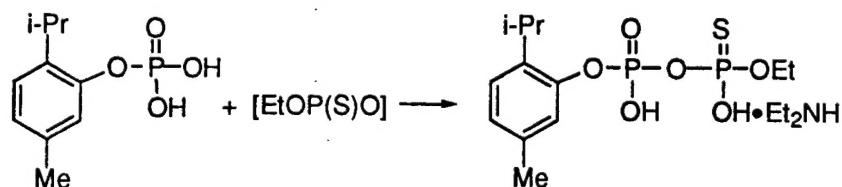




Fragmentation of the thiophosphoramidic acid occurred readily at mild temperatures ( typically 3 hours at 80<sup>0</sup>) and provided the expected mixed pyrophosphate. This was shown to be a first-order process as required by the unimolecular mechanism involving release of alkyl metathiophosphate. Kinetic isotope effects measurements again showed that the dipolar form was the actual species undergoing the fragmentation<sup>8</sup>. When an alcohol was present as a trapping agent, the intermediate was intercepted and a dialkyl thiophosphate was formed as the only detectable product.

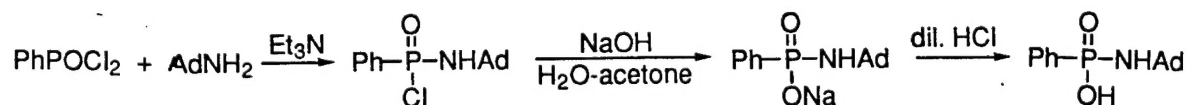


It was also possible to perform thiophosphorylation of the surface of silica gel by this method. Novel monothiopyrophosphates (e.g.,6) were prepared by phosphorylation of monoalkyl phosphates.

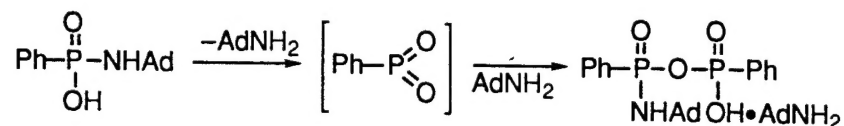


### C. Generation of Phenyl Dioxophosphorane by Fragmentation of a Phenylphosponamidic Acid.

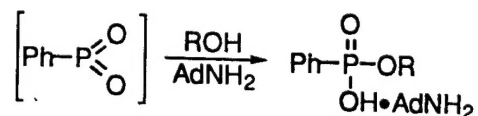
It was visualized that the method developed for the generation of alkyl metaphosphates and metathiophosphates from amidic acid derivatives was capable of further extension to the generation of the analogous P-aryl or P-alkyl derivatives, which are better named as dioxophosphoranes. As for the phosphate derivatives, the presence of a large bulky group on nitrogen seemed essential to guide the reaction into the unimolecular mechanism, and to this end the model compound N-(1-adamantyl) phenylphosponamidic acid was synthesized. This was accomplished easily by reacting the commercially available phenylphosphonic dichloride with one mole of adamantylamine along with one mole of triethylamine. The product was then hydrolyzed to give the phosphonamidic acid<sup>9</sup>.



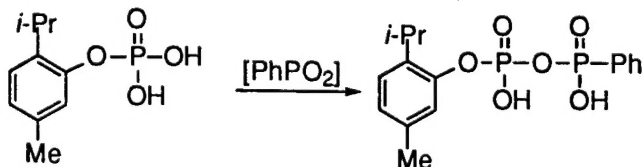
Thermal fragmentation of the phosphonamidic acid occurred with great ease; in 1,2-dichloroethane it was complete in 30 min. at 50°. The only product was the anhydride **7**.



The fragmentation followed the expected first-order kinetics, and when an alcohol was present the product was the monoalkyl ester of phenylphosphonic acid.



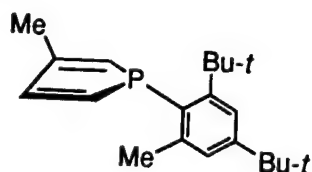
It can be concluded that the phosphonamidic acid fragmentation has indeed occurred with release of phenyl dioxophosphorane as a transient intermediate. This is a much simpler method for the generation of this species than others that have been reported, in that the required starting material is easily prepared and the conditions for the fragmentation are quite mild. Utility for the new method was demonstrated by using it to prepare a novel mixed phosphonic-phosphoric anhydride (**8**) by phosphorylation of a phosphate when present as a trapping agent.



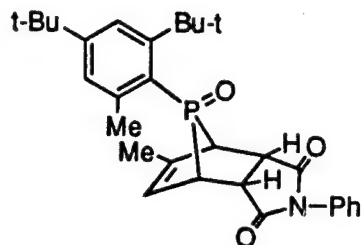
It was also shown that silica gel could be phosphorylated by generating phenyl dioxophosphorane in its presence. In the future, this new method should be extended if possible to include the generation of other dioxophosphoranes, since little is known about this transient species and its synthetic utility.

#### D. Synthesis of Phospholes and 7-Phosphanorbornenes with Large P-Substituents.

The earlier grant period<sup>1</sup> dealt heavily with the 7-phosphanorbornene ring system as a framework for construction of precursors of low-coordination species. Some additional work has been conducted with this system, and with the phosphole system that is required in its construction. Here the emphasis has been on the synthesis of derivatives with very large substituents on phosphorus, which might be expected to increase the kinetic stability of the low coordination species. The presence of large substituents on phospholes is also of interest but more from a theoretical standpoint: it has been predicted by computational studies that if phospholes can be forced into a higher degree of planarity at phosphorus they should be capable of increased electron delocalization<sup>10</sup>. We have successfully prepared a phosphole with a 2,4-di-tert-butyl-6-methylphenyl substituent, and found definite indications of strong steric effects on phosphorus<sup>11</sup>. The normal rotation around the P-aryl bond was prevented, and a conformation adopted with the smaller 6-methyl group under the phosphole ring plane, leaving the larger 2-tert-butyl on the less crowded face where the phosphorus lone pair resides. This conformation is shown as 9.



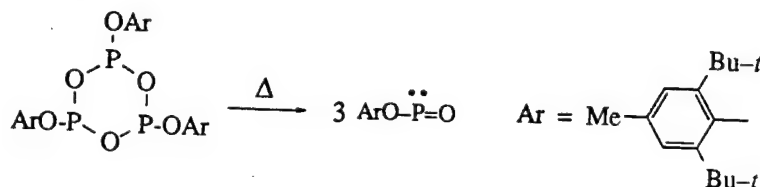
The photoelectron spectrum was useful in showing an increase in the delocalization; all phospholes studied to date have about the same ionization energy as their tetrahydro counterparts since little delocalization is present, but phosphole 9 had an appreciably higher ionization energy (7.9 eV) than the tetrahydro derivative (7.55 eV). The value for 9 is the lowest ever recorded for a phosphole. This is consistent with an increase in the delocalization. The P-oxide of the phosphole gave rise to the 7-phosphanorbornene ring system through dimerization or through Diels-Alder reaction with N-phenylmaleimide (as in 10). In work still to be performed, oxygen insertion into a P-C bond will be carried out, so as to give the 2,3-oxaphosphabicyclo[2.2.2]octene ring system; on thermolysis, the aryl dioxophosphorane should be liberated. Hopefully, some increased stability of this species can be found by spectral studies at low temperature. This work will be continued in a collaboration with Prof. Gyorgy Keglevich at the Technical University of Budapest, Hungary.



In recent work by Prof. Keglevich in Budapest, phospholes with the 2,4,6-tri-isopropylphenyl and 2,4,6-tri-*tert*-butyl substituents have been prepared and subjected to X-ray crystallographic analysis. Both showed the expected partial flattening of the phosphorus pyramid, which is more pronounced in the latter. Bond lengths are changed in the expected directions from the increased delocalization. Both phospholes have been oxidized and converted to 7-phosphanorbornene derivatives, which are to be used as precursors of the corresponding hindered aryl dioxophosphoranes.

#### E. Generation of an Aryl Phosphenite By Cracking of a Trioxatriphosphorinane.

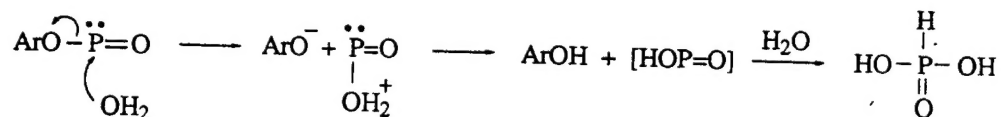
Some work initiated during the last grant period<sup>1</sup> on a new technique for generation of the 2-coordinate phosphenite system was successfully completed. Phosphenites are mentioned in the literature but there is no direct proof of their existence by spectral or other methods. We were able to generate 2,6-di-*tert*-butyl-4-methylphenyl phosphenite by thermal cracking of a well-known trimeric form, having the 1,3,5,2,4,6-trioxatriphosphorinane ring system, and proceeded to characterize the species at low temperature by <sup>31</sup>P NMR, IR and UV spectroscopy<sup>12</sup>.



In continuing this work, we devised a new method for preparing the cyclic trimer, based on the reaction of the aryl phosphorodichloridite with silver oxide<sup>13</sup> but were not successful in preparing the alkyl derivatives. Some new reactions of the trimer were also studied, including oxidation reactions, addition of sulfur, and addition of an ortho quinone.

The trimer was cracked at 300-350<sup>0</sup> and 10<sup>-6</sup>mm in an apparatus allowing the cracking gas to condense directly on a finger chilled by liquid nitrogen (-195<sup>0</sup>)<sup>14</sup>. At this temperature the material is monomeric, but it was shown that dimerization occurred on warming. The dimer ultimately was converted to the trimer. The phosphenite while at -195<sup>0</sup> was sprayed with a water solution, leading

to formation of the expected H-phosphonate from addition of water to the P=O group. However a second product was found to be phosphorous acid, which is believed this forms after nucleophilic displacement of the aryloxy group, a new observation for a phosphenite. Water then presumably adds to the generated intermediate.



Similarly, spraying with ethanol led to the expected ethyl ester of the H-phosphonate but also to diethyl H-phosphonate from the displacement. The phosphenite was also shown to be in equilibrium with the dimer at room temperature, attesting to its increased stability. The dimer in turn formed the trimer, so that a mixture of all three was observed when examined by  $^{31}\text{P}$  NMR at room temperature. Such mixtures typically contained 3-5% of the monomer.

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